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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a positive electrode material for non-aqueous electrolyte secondary batteries which makes charge/discharge electricity in a high rate possible, has high capacity, has excellent durability in charge/discharge- electricity cycle, and has high safety.
SOLUTION: In the lithium secondary battery equipped with the positive electrode active material layer which has a lithium transition metal complex oxide as a principal component, the above lithium transition metal complex oxide is constituted of a mixture with a lithium-nickel-manganese-M complex having R-3m rhomb structure expressed by $Li_xNi_yMn_{1-y-z}M_zO_2$ (however, x is $0.9\leq x\leq 1.2$, y is $0.40\leq y\leq 0.60$, and z is $0\leq z\leq 0.2$, and M is chosen from either of Fe, Co, Cr, or Al), and a lithium-manganese spinel complex oxide having a Fd-3m spinel structure and expressed with $Li_pMn_2O_4$ (however, p is $1\leq p\leq 1.3$).

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CLAIMS

[Claim(s)]
[Claim 1] In the lithium secondary battery equipped with the positive-active-material layer which uses a lithium transition-metals multiple oxide as a principal component The above-mentioned lithium transition-metals multiple oxide is LixNiyMn1-y-zMzO2 (however, x is [0.40<=y<=0.60 and z of 0.9<=x<=1.2 and y] 0<=z<=0.2, and M is chosen from Fe, Co, Cr, or aluminum atom.). It has Fd3m Spinel structure and is [the lithium-nickel-manganese-M multiple oxide expressed and] LipMn 2O4 (however, p is 1<=p<=1.3.). The lithium secondary battery characterized by consisting of mixture with the lithium-manganese spinel multiple oxide expressed.
[Claim 2] The lithium secondary battery according to claim 1 characterized by the content of the above-mentioned lithium-nickel-manganese-M multiple oxide in the above-mentioned mixture being 30 - 70 % of the weight.
[Claim 3] The lithium secondary battery according to claim 1 or 2 characterized by the fine-particles press consistencies of the above-mentioned mixture being three or more 2.7 g/cm.
[Claim 4] The lithium secondary battery according to claim 1, 2, or 3 characterized by the above-mentioned lithium-nickel-manganese-M multiple oxide being R-3m rhombohedron structure.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the lithium secondary battery equipped with the improved positive-active-material layer.
[0002]
[Description of the Prior Art] Small and the expectation for the nonaqueous electrolyte rechargeable battery which is lightweight and has a high energy consistency are growing as portable-izing of a device and cordless-ization progress in recent years. The multiple oxide of lithiums, such as LiCoO2, LiNiO2, LiMn2O4, and LiMnO2, and transition metals is known by the active material for nonaqueous electrolyte rechargeable batteries.
[0003] In it, as a cheap ingredient with safety especially high recently and, research of the multiple oxide of a lithium and manganese is done briskly, these are used for positive active material, and development of the nonaqueous electrolyte rechargeable battery of the high voltage by combining negative-electrode active materials, such as occlusion and a carbon material which can be emitted, and a high energy consistency is furthered in the lithium.
[0004] Generally, the positive active material used for a nonaqueous electrolyte rechargeable battery becomes the lithium which is the main active material from the multiple oxide which made transition metals including cobalt, nickel, and manganese dissolve. With classes of the transition metals used, the electrode characteristics, such as electric capacity, reversibility, operating potential, and safety, change. For example, the nonaqueous electrolyte rechargeable battery which used for positive active material R-3m rhombohedron rock salt stratified multiple oxide which made cobalt and nickel dissolve like LiCoO2 and LiNi0.8Co 0.2O2 shows good reversibility in high electrical-potential-difference regions, such as 2.5-4.3V, while being able to attain 140 - 160 mAh/g and 180 - 200 mAh/g, and a comparatively high capacity consistency, respectively.
[0005]
[Problem(s) to be Solved by the Invention] However, when a cell is warmed, since the problem on which a cell tends to generate heat by the reaction of the positive active material at the time of charge and an electrolytic-solution solvent, the cobalt used as a raw material, and nickel are expensive, there is a problem to which the cost of an active material becomes high.
[0006] Although a cell cannot generate heat comparatively easily due to the reaction of the positive active material at the time of charge, and an electrolytic-solution solvent, compared with a cobalt system and a nickel system active material with an above-mentioned capacity, with 100 - 120 mAh/g, the nonaqueous electrolyte rechargeable battery which used for the active material the spinel mold multiple oxide which consists of LiMn 2O4 which uses on the other hand comparatively cheap manganese as a raw material is low, and has the technical problem that charge-and-discharge cycle endurance is scarce.
[0007] Instead of using these independent lithium-transition-metals multiple oxides as positive active material, mixing the a kind of lithium [at least]-transition-metals multiple oxide chosen from the group which consists of LiMnO2, LiNiO2 and LiCoO2, and LiMn 2O4 of orthorhombic system is proposed by JP,9-180718,A. The cell using this mixture originates in LiMnO2, and has

the problem which runs short of charge-and-discharge cycle endurance. Moreover, $LiMnO_2$ also has the problem that the charge-and-discharge capacity in a high rate is low.
[0008] Moreover, the lithium secondary battery which consists of $LiMn_2O_4$ and three-sort mixture of $LiNiO_2$ and $LiCoO_2$ is proposed by JP,11-3698,A. The cell using this $LiMn_2O_4$ and the three-sort mixture of $LiNiO_2$ and $LiCoO_2$ originates in use of $LiNiO_2$ and $LiCoO_2$, and has the problem which is not enough.
[0009] Made in order that this invention might solve such a technical problem, the charge and discharge in a high rate are possible for the purpose, and its capacity is high, and it is to offer a nonaqueous electrolyte rechargeable battery with the sufficient high energy consistency and sufficient high current discharge property using the positive-electrode ingredient for nonaqueous electrolyte rechargeable batteries of the Takayasu all nature excellent in charge-and-discharge cycle endurance.
[0010]
[Means for Solving the Problem] In the lithium secondary battery equipped with the positive-active-material layer to which this invention uses a lithium transition-metals multiple oxide as a principal component in order to attain the above-mentioned purpose The above-mentioned lithium transition-metals multiple oxide is $Li_xNi_yMn_{1-y-z}M_zO_2$ (however, x is [$0.40<=y<=0.60$ and z of $0.9<=x<=1.2$ and y] $0<=z<=0.2$, and M is chosen from Fe, Co, Cr, or aluminum atom.). It has Fd3m Spinel structure and is [the lithium-nickel-manganese-M multiple oxide expressed and] $Li_pMn_2O_4$ (however, p is $1<=p<=1.3$.). It is characterized by consisting of mixture with the lithium-manganese spinel multiple oxide expressed.
[0011] As for the above-mentioned lithium-nickel-manganese-M multiple oxide, in this invention, it is desirable that it is R3-m rhombohedron structure. In addition, since it is hard coming to take stable R-3m rhombohedron structure with y being less than 0.40, it is not desirable. Moreover, since safety will fall if y exceeds 0.60, it is not desirable. As for y, 0.45-0.55 are adopted especially preferably. As for x, $0.9<=x<=1.2$ is adopted for a capacity manifestation.
[0012] Improvement in charge-and-discharge cycle endurance, safety, capacity, etc. can be aimed at by adding one atom of Fe, Co, Cr, and aluminum further to the above-mentioned lithium-nickel-manganese M multiple oxide. the addition z of M atom -- 0-0.2 -- it is -- desirable -- 0.01 to 0.18 -- it is 0.05-0.16 especially preferably.
[0013] although another above-mentioned lithium multiple oxide used by this invention is a lithium-manganese spinel multiple oxide which has Fd3m Spinel structure and is expressed with $Li_pMn_2O_4$ (however, p is $1<=p<=1.3$.) -- the manganese element in this manganese spinel -- the alkaline-earth-metal elements and transition-metals elements other than manganese -- having -- 2-10-mol % -- charge-and-discharge cycle endurance can be raised by permuting. Magnesium, aluminum, iron, and chromium are chosen as a desirable permutation element of the manganese in a manganese spinel.
[0014] As for the content of the above-mentioned lithium-nickel-manganese-M multiple oxide in the above-mentioned mixture, in this invention, it is desirable that it is 30 - 70 % of the weight. Since the capacity of a lithium cell falls that the above-mentioned content is less than 30 % of the weight or charge-and-discharge cycle endurance falls, it is not desirable. Moreover, since the discharge capacity in a high rate will fall or a discharge average electrical potential difference will fall if the above-mentioned content exceeds 70 % of the weight, it is not desirable. Especially the desirable above-mentioned content is 40 - 60 % of the weight.
[0015] As for the mixture powder of the above-mentioned multiple oxide, in this invention, it is desirable that the fine-particles press consistencies when carrying out press restoration only of the powder by the pressure of 1 t/cm2 are three or more 2.7 g/cm. According to this, mixture is made with a slurry, and coating and desiccation, and when it presses, capacity per volume can be made high at charge collector aluminum foil. Especially desirable fine-particles press consistencies are three or more 2.9 g/cm. A three or more 2.7 g/cm fine-particles press consistency is attained by rationalizing the particle size distribution of mixture fine particles. That is, width of face is in particle size distribution, the volume fraction of few particle size is 20 - 50%, and densification can be attained by narrowing particle size distribution of the diameter of a large drop etc.

[0016] If the mixture of this invention is used, from the case where each independent lithium transition-metals multiple oxide used for mixing is used, the charge and discharge in a high rate are possible, and capacity and the cell engine performance whose balance of safety improved can be discovered. Moreover, capacity and the cell engine performance which excelled [list / safety] in charge-and-discharge cycle stability can be obtained from the case where the same positive active material as the transition-metals element content which consisted of an independent lithium transition-metals compound, and was used for mixing is used. Although the cause by which this physical mixture is superior to the independent matter is not clear, a lithium-nickel-manganese-M multiple oxide (nickel/Mn=0.6 / 0.4 - 0.4/0.6) has specially high safety, and since the manifestation nature of capacity is comparatively good, it is thought that the synergistic effect was discovered with mixing.

[0017]

[Embodiment of the Invention] As a process of LixNiyMn1-y-zMzO2 (lithium-nickel-manganese-M multiple oxide) which the crystal structure used for this invention becomes from R-3m of rhombohedron, calcinating the mixture of a manganese compound, a lithium compound, and a nickel compound 500-1000 degrees C of solid phase techniques under an inert gas ambient atmosphere or in atmospheric air, for example and a 500-850-degree C fused salt method are mentioned.

[0018] Moreover, the lithium-nickel-manganese-M multiple oxide with which the crystal structure used for this invention consists of rhombohedron stratified rock salt type structure can be obtained by the fused salt method which adds a nickel-manganese-metallic element M content compound in calcinating the mixture of the multiple oxide or compound hydroxide which consists for example, of a nickel-manganese-metallic element, a manganese compound, and a lithium compound 500-1000 degrees C of solid phase techniques under an oxygen gas content ambient atmosphere, and 500-850-degree C lithium content fused salt.

[0019] As a source raw material of nickel, oxides (NiO etc.), a hydroxide (NiOH), an oxy-hydroxide (NiOOH), etc. are mentioned. As a source raw material of manganese, the hydrate of oxides (Mn 2O3, MnO, MnO2, etc.) and these oxides, an oxy-hydroxide, etc. are mentioned. As a source raw material of manganese, the compound of trivalent manganese is more desirable. These source raw materials of manganese may be used independently, and may use two or more sorts together.

[0020] As a source raw material of (a metallic element M), a simple substance metal, a hydroxide, an oxide, an oxy-hydroxide, a chloride, a nitrate, etc. are used. The source raw material of these the (metallic elements M) may be used independently, and may use two or more sorts together.

[0021] mixing carbon system electric conduction material and binding material, such as acetylene black, a graphite, and ketch en black, to the powder of the mixture of this invention -- a positive electrode -- a mixture is formed. Polyvinylidene fluoride, polytetrafluoroethylene, a polyamide, a carboxymethyl cellulose, acrylic resin, etc. are used for binding material. the slurry which consists of the solvent or dispersion medium of the powder of the mixture of this invention, electric conduction material, binding material, and binding material -- positive-electrode charge collectors, such as aluminium foil, -- coating - it dries and rolls [press] out and a positive-active-material layer is formed on a positive-electrode charge collector.

[0022] In the lithium cell of this invention, a carbonate is desirable as a solvent of an electrolytic solution. a carbonate -- the shape of annular and a chain -- all can be used. Propylene carbonate, ethylene carbonate, etc. are illustrated as an annular carbonate. As a chain-like carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, etc. are illustrated.

[0023] In this invention, it is independent in the above-mentioned carbonate, or two or more sorts can be mixed and used. Moreover, you may use it, mixing with other solvents. Moreover, if a chain-like carbonate and an annular carbonate are used together depending on the ingredient of a negative-electrode active material, a discharge property, cycle endurance, and charge-and-discharge effectiveness may be improvable. Moreover, it is good also as a gel polymer electrolyte by adding a vinylidene fluoride-hexafluoropropylene copolymer (for example, Atochem KAINA) and a vinylidene fluoride-perfluoro propyl vinyl ether copolymer to these organic solvents, and

adding the following solute.
[0024] It is desirable to use as a solute any one or more sorts of the lithium salt which makes an anion ClO4-, CF3SO3-, BF4-, PF6-, AsF6-, SbF6-, CF3CO2-, 2 (CF3SO2)N-, etc. As for an above-mentioned electrolytic solution or an above-mentioned polymer electrolyte, it is desirable to add the electrolyte which consists of lithium salt by the concentration of 0.2-2.0 mols/l. to the above-mentioned solvent or a solvent content polymer. If it deviates from this range, ionic conductivity will fall and electrolytic electrical conductivity will fall. 0.5 - 1.5 mol/l is selected more preferably. Porosity polyethylene and a porosity polypropylene film are used for a separator.
[0025] The negative-electrode active material in this invention is the ingredient which emits [occlusion and] a lithium ion. Although especially the ingredient that forms these negative-electrode active materials is not limited, a lithium metal, a lithium alloy, a carbon material, a periodic table 14, the oxide that made 15 groups' metal the subject, a carbon compound, a silicon carbide compound, a silicon oxide compound, a titanium sulfide, a boron carbide compound, etc. are mentioned, for example.
[0026] What pyrolyzed the organic substance on various pyrolysis conditions as a carbon material, an artificial graphite, a natural graphite, a soil graphite, expanded graphite, a scale-like graphite, etc. can be used. Moreover, the compound which makes the tin oxide a subject can be used as an oxide. Copper foil, a nickel foil, etc. are used as a negative-electrode charge collector.
[0027] As for the positive electrode and negative electrode in this invention, it is desirable to knead an active material with an organic solvent, to consider as a slurry, to apply, dry and press this slurry in a metallic foil charge collector, and to obtain it to it. There is especially no constraint in the configuration of the lithium cell of this invention. The shape of a sheet (the shape of so-called film), the letter of folding, a winding mold closed-end cylindrical shape, a carbon button form, etc. are chosen according to an application.
[0028]
[Example] Next, although this invention is explained about the concrete examples 1-8 and the examples 1-4 of a comparison, this invention is not limited to these examples.
[0029] <<example 1>> Coprecipitation of aqueous ammonia and the sodium-hydroxide water solution was added and carried out to the nickel sulfate and the manganese-sulfate (mole ratio 1:1) mixed water solution, and the nickel-manganese coprecipitation hydroxide (nickel: manganese atomic ratio =1:1) was obtained by heating and desiccation at 150 degrees C. This nickel-manganese coprecipitation hydroxide was calcinated and ground in atmospheric air at 550 degrees C, and nickel-manganic acid ghost powder was obtained. This nickel-manganic acid ghost powder and lithium-carbonate powder were mixed, it calcinated and ground in nitrogen-gas-atmosphere mind at 800 degrees C, and LiNi0.5Mn 0.5O2 with a mean particle diameter of 4 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. Moreover, the electrolytic manganese dioxide powder and lithium-carbonate powder were blended dryly, 800 degrees C was calcinated in atmospheric air for 15 hours, grinding and classification of were done, and 2OLi1.05Mn4 powder with a mean particle diameter of 7 micrometers was obtained. X-ray diffraction analysis by CuKalpha of this powder showed that it was Fd3m Spinel structure. When LiNi0.5Mn 0.5O2 and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this mixture powder was carried out by the pressure of 1 t/cm2 and the fine-particles press consistency was calculated from the volume and weight, it was 2.90 g/cm3. N-methyl pyrrolidone ******** ball mill mixing of this mixture powder, acetylene black, and polyvinylidene fluoride was carried out by the weight ratio of 83/10/7, and it considered as the slurry. This slurry was applied on the aluminium foil positive-electrode charge collector with a thickness of 20micro, it dried at 150 degrees C, and N-methyl pyrrolidone was removed. Roll press rolling was carried out to after an appropriate time, and the positive-electrode object was acquired. A metal lithium foil with a thickness of 300micro is used for a separator at a negative electrode using porosity polyethylene with a thickness of 25micro, a nickel foil is used for a negative-electrode charge collector, and it is 1M in the electrolytic solution. LiPF6/EC+DEC

(1:1) is used and it is ****** in an argon glove compartment about coin cel 2030 mold. And the bottom of a 25-degree C temperature ambient atmosphere is charged by 1mA termination electrical-potential-difference 4.3V. While discharging to 3.0V in 5mA (discharge rate 1C) of constant current and investigating a high current discharge property It charged by 1mA termination electrical-potential-difference 4.3V, the charge-and-discharge cycle trial which discharges to 3.0V in 1mA (discharge rate 0.2C) of constant current was performed 20 times, and it asked for the capacity maintenance factor from the ratio of the initial discharge capacity after 2 times charge and discharge, and the discharge capacity after 20 times charge and discharge. Moreover, for cell safety evaluation, the cel after 4.3V charge was disassembled and exoergic initiation temperature in case the positive electrode was put into the well-closed container and carries out a temperature up to a sample using nothing and differential-scanning-calorimetry equipment with an electrolytic-solution solvent was searched for. Consequently, for initial capacity, 124 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 227 degrees C 93% 92%.

[0030] <<example 2>> LiNi0.6Mn 0.4O2 which set the nickel of a lithium-nickel-manganese multiple oxide and the atomic ratio of manganese to 0.60:0.40, and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 130 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 221 degrees C 94% 92%.

[0031] <<example 3>> The nickel of a lithium-nickel-manganese multiple oxide and the atomic ratio of manganese mixed LiNi0.5Mn 0.5O2 which is 0.50:0.50, and Li1.05Mn 2O4 at a rate of 40:60 by the weight ratio, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 122 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 220 degrees C 94% 93%.

[0032] <<example 4>> LiNi0.55Mn 0.45O2 which set the nickel of a lithium-nickel-manganese multiple oxide and the atomic ratio of manganese to 0.55:0.45, and Li1.05Mn 2O4 were mixed at a rate of 30:70 by the weight ratio, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 121 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 220 degrees C 94% 94%.

[0033] <<example 5>> Replaced with the nickel sulfate and manganese-sulfate (mole ratio 1:1) mixed water solution of the above-mentioned example 1, and the nickel sulfate, the manganese sulfate, and the cobalt sulfate (mole ratio 9:9:2) mixed water solution were used, and also LiNi0.45Mn0.45Co 0.1O2 with a mean particle diameter of 5 micrometers was compounded as positive active material like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. When LiNi0.45Mn0.45Co 0.1O2 and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this mixture powder was carried out by the pressure of 1 t/cm2 and the fine-particles press consistency was calculated from the volume and weight, it was 2.95 g/cm3. The positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 128 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 226 degrees C 95% 93%.

[0034] <<example 6>> Replaced with the nickel sulfate and manganese-sulfate (mole ratio 1:1) mixed water solution of the above-mentioned example 1, and the nickel sulfate, the manganese sulfate, and the chromium-sulfate (mole ratio 9:9:2) mixed water solution were used, and also LiNi0.45Mn0.45Cr 0.1O2 with a mean particle diameter of 5 micrometers was compounded as positive active material like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. When LiNi0.45Mn0.45Cr 0.1O2 and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this mixture powder was carried out by the pressure of 1 t/cm2 and the fine-particles press consistency was calculated from the volume and weight, it

was 2.92 g/cm3. The positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 126 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 230 degrees C 95% 93%.

[0035] <<example 7>> Replaced with the nickel sulfate and manganese-sulfate (mole ratio 1:1) mixed water solution of the above-mentioned example 1, and the nickel sulfate, the manganese sulfate, and the iron-sulfate (mole ratio 9:9:2) mixed water solution were used, and also LiNi0.45Mn0.45Fe 0.1O2 with a mean particle diameter of 5 micrometers was compounded as positive active material like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. When LiNi0.45Mn0.45Fe 0.1O2 and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this mixture powder was carried out by the pressure of 1 t/cm2 and the fine-particles press consistency was calculated from the volume and weight, it was 2.90 g/cm3. The positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 123 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 231 degrees C 94% 93%.

[0036] <<example 8>> Replaced with the nickel sulfate and manganese-sulfate (mole ratio 1:1) mixed water solution of the above-mentioned example 1, and the nickel sulfate, the manganese sulfate, and the aluminum-sulfate (mole ratio 9:9:2) mixed water solution were used, and also LiNi0.45Mn0.45aluminum 0.1O2 with a mean particle diameter of 5 micrometers was compounded as positive active material like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. When LiNi0.45Mn0.45aluminum 0.1O2 and Li1.05Mn 2O4 were mixed at a rate of 50:50 by the weight ratio, the hydraulic press of this mixture powder was carried out by the pressure of 1 t/cm2 and the fine-particles press consistency was calculated from the volume and weight, it was 2.87 g/cm3. The positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 124 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 233 degrees C 94% 93%.

[0037] <Example 1 of a comparison> LiNi0.5Mn 0.5O2 used in the above-mentioned example 1 was used independently, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 128 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 230 degrees C 92% 85%.

[0038] <Example 2 of a comparison> Coprecipitation of aqueous ammonia and the sodium-hydroxide water solution was added and carried out to the nickel sulfate and the manganese-sulfate (mole ratio 0.70:0.30) mixed water solution, and the nickel-manganese coprecipitation hydroxide (nickel: manganese atomic ratio =0.70:0.30) was obtained by heating and desiccation at 150 degrees C. This nickel-manganese coprecipitation hydroxide was calcinated and ground in atmospheric air at 550 degrees C, and nickel-manganic acid ghost powder was obtained. This nickel-manganic acid ghost powder and lithium-hydroxide powder were mixed, and it calcinated at 480 degrees C, it calcinated and ground at 800 degrees C in atmospheric air further, and LiNi0.7Mn 0.3O2 was compounded. This LiNi0.7Mn 0.3O2 was used independently, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 167 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 200 degrees C 91% 86%.

[0039] <Example 3 of a comparison> Li1.05Mn 2O4 used in the above-mentioned example 1 was used independently, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 117 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 220 degrees C 93% 94%.

[0040] <Example 4 of a comparison> Coprecipitation of aqueous ammonia and the sodium-

hydroxide water solution was added and carried out to the nickel sulfate and the manganese-sulfate (mole ratio 0.25:0.75) mixed water solution, and the nickel-manganese coprecipitation hydroxide (nickel: manganese atomic ratio =0.25:0.75) was obtained by heating and desiccation at 150 degrees C. This nickel-manganese coprecipitation hydroxide was calcinated and ground in atmospheric air at 550 degrees C, and nickel-manganic acid ghost powder was obtained. This nickel-manganic acid ghost powder and lithium-hydroxide powder were mixed, and it calcinated at 480 degrees C, it calcinated and ground at 800 degrees C in nitrogen-gas-atmosphere mind further, and LiNi0.25Mn 0.75O2 was compounded. This LiNi0.25Mn 0.75O2 was used independently, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Consequently, for initial capacity, 119 mAh/g, and 1C capacity / 0.2C capacity was [the exoergic initiation temperature of the capacity maintenance factor] 230 degrees C 87% 83%.

[0041] As reference, the multiple oxide used in the above-mentioned examples 1-8 and the examples 1-4 of a comparison and an evaluation result are collectively shown in degree table.

[Table 1]

	第1活物質	混合比(%)	第2活物質	混合比(%)	容量(mAh/g)	1C容量/0.2C容量(%)	容量維持率(%)	発熱開始温度(℃)
実施例1	$LiNi_{0.50}Mn_{0.50}O_2$	50	$Li_{1.05}Mn_2O_4$	50	124	92	93	227
実施例2	$LiNi_{0.60}Mn_{0.40}O_2$	50	$Li_{1.05}Mn_2O_4$	50	130	92	94	221
実施例3	$LiNi_{0.50}Mn_{0.50}O_2$	40	$Li_{1.05}Mn_2O_4$	60	122	93	94	220
実施例4	$LiNi_{0.55}Mn_{0.45}O_2$	30	$Li_{1.05}Mn_2O_4$	70	121	94	94	220
実施例5	$LiNi_{0.45}Mn_{0.45}Co_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	128	93	95	226
実施例6	$LiNi_{0.45}Mn_{0.45}Cr_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	126	93	95	230
実施例7	$LiNi_{0.45}Mn_{0.45}Fe_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	123	93	94	231
実施例8	$LiNi_{0.45}Mn_{0.45}Al_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	124	93	94	233
比較例1	$LiNi_{0.50}Mn_{0.50}O_2$	100	—		128	85	92	230
比較例2	$LiNi_{0.70}Mn_{0.30}O_2$	100	—		167	86	91	200
比較例3	—		$Li_{1.05}Mn_2O_4$	100	117	94	93	220
比較例4	$LiNi_{0.25}Mn_{0.75}O_2$	100	—		119	83	87	230

[0042]
[Effect of the Invention] As explained above, in the lithium secondary battery equipped with the positive-active-material layer which uses a lithium transition-metals multiple oxide as a principal component, by using the mixture of the multiple oxide of this invention for a lithium transition-metals multiple oxide, the charge and discharge in a high rate are possible, and capacity and the cell engine performance whose balance of safety improved can be discovered from the case

where each independent lithium transition-metals multiple oxide used for mixing is used.
[0043] Moreover, capacity and the cell engine performance which excelled [list / safety] in charge-and-discharge cycle stability can be obtained from the case where the same positive active material as the transition-metals element content which consisted of an independent lithium transition-metals compound, and was used for mixing is used.

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(54)【発明の名称】 リチウム二次電池

(57)【要約】

【課題】 ハイレートでの充放電が可能で、容量が高く、充放電サイクル耐久性に優れた高安全性の非水電解液二次電池用正極材料を得る。

【解決手段】 リチウム遷移金属複合酸化物を主成分とする正極活物質層を備えたリチウム二次電池において、上記リチウム遷移金属複合酸化物に、Ｒ－３ｍ菱面体構造を有し$Li_xNi_yMn_{1-y-z}M_zO_2$（ただし、ｘは０．９≦ｘ≦１．２、ｙは０．４０≦ｙ≦０．６０、ｚは０≦ｚ≦０．２であり、ＭはＦｅ，Ｃｏ，Ｃｒ，Ａｌ原子のいずれかから選択される。）で表されるリチウム－ニッケル－マンガン－Ｍ複合酸化物と、Ｆｄ３ｍスピネル構造を有し$Li_pMn_2O_4$（ただし、ｐは１≦ｐ≦１．３である。）で表されるリチウム－マンガンスピネル複合酸化物との混合物を用いる。

【特許請求の範囲】

【請求項１】　リチウム遷移金属複合酸化物を主成分とする正極活物質層を備えたリチウム二次電池において、上記リチウム遷移金属複合酸化物が、$Li_xNi_yMn_{1-y-z}M_zO_2$（ただし、ｘは０．９≦ｘ≦１．２、ｙは０．４０≦ｙ≦０．６０、ｚは０≦ｚ≦０．２であり、ＭはＦｅ，Ｃｏ，Ｃｒ，Ａｌ原子のいずれかから選択される。）で表されるリチウム－ニッケル－マンガン－Ｍ複合酸化物と、Ｆｄ３ｍスピネル構造を有し、$Li_pMn_2O_4$（ただし、ｐは１≦ｐ≦１．３である。）で表されるリチウム－マンガンスピネル複合酸化物との混合物からなることを特徴とするリチウム二次電池。

【請求項２】　上記混合物中の上記リチウム－ニッケル－マンガン－Ｍ複合酸化物の含有量が３０～７０重量％であることを特徴とする請求項１記載のリチウム二次電池。

【請求項３】　上記混合物の粉体プレス密度が２．７ｇ／cm^3以上であることを特徴とする請求項１または２記載のリチウム二次電池。

【請求項４】　上記リチウム－ニッケル－マンガン－Ｍ複合酸化物がＲ－３ｍ菱面体構造であることを特徴とする請求項１，２または３に記載のリチウム二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、改良された正極活物質層を備えたリチウム二次電池に関する。

【０００２】

【従来の技術】近年、機器のポータブル化、コードレス化が進むにつれ、小型、軽量でかつ高エネルギー密度を有する非水電解液二次電池に対する期待が高まっている。非水電解液二次電池用の活物質には、$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$、$LiMnO_2$などのリチウムと遷移金属の複合酸化物が知られている。

【０００３】その中で特に最近では、安全性が高くかつ安価な材料として、リチウムとマンガンの複合酸化物の研究が盛んに行なわれており、これらを正極活物質に用いて、リチウムを吸蔵、放出することができる炭素材料等の負極活物質とを組み合わせることによる、高電圧、高エネルギー密度の非水電解液二次電池の開発が進められている。

【０００４】一般に、非水電解液二次電池に用いられる正極活物質は、主活物質であるリチウムにコバルト、ニッケル、マンガンをはじめとする遷移金属を固溶させた複合酸化物からなる。その用いられる遷移金属の種類によって、電気容量、可逆性、作動電圧、安全性などの電極特性が異なる。例えば、$LiCoO_2$、$LiNi_{0.8}Co_{0.2}O_2$のようにコバルトやニッケルを固溶させたＲ－３ｍ菱面体岩塩層状複合酸化物を正極活物質に用いた非水電解液二次電池は、それぞれ１４０～１６０ｍＡｈ／ｇおよび１８０～２００ｍＡｈ／ｇと比較的高い容量密度を達成できるとともに、２．５～４．３Ｖといった高い電圧域では良好な可逆性を示す。

【０００５】

【発明が解決しようとする課題】しかしながら、電池を加温した際に、充電時の正極活物質と電解液溶媒との反応により電池が発熱し易い問題や、原料となるコバルトやニッケルが高価であるので活物質のコストが高くなる問題がある。

【０００６】一方、比較的安価なマンガンを原料とする$LiMn_2O_4$からなるスピネル型複合酸化物を活物質に用いた非水電解液二次電池は、充電時の正極活物質と電解液溶媒との反応により電池が比較的発熱しにくいものの、容量が上述のコバルト系およびニッケル系活物質にくらべ１００～１２０ｍＡｈ／ｇと低く、充放電サイクル耐久性が乏しいという課題がある。

【０００７】これらの単独のリチウム－遷移金属複合酸化物を正極活物質として使用する代わりに、斜方晶系の$LiMnO_2$と、$LiNiO_2$、$LiCoO_2$および$LiMn_2O_4$からなる群より選択される少なくとも一種のリチウム－遷移金属複合酸化物を混合することが特開平９－１８０７１８号公報に提案されている。かかる混合物を用いた電池は$LiMnO_2$に起因して、充放電サイクル耐久性が不足する問題がある。また、$LiMnO_2$はハイレートでの充放電容量が低い問題もある。

【０００８】また、特開平１１－３６９８号公報には、$LiMn_2O_4$、$LiNiO_2$および$LiCoO_2$の３種混合物からなるリチウム二次電池が提案されている。かかる$LiMn_2O_4$、$LiNiO_2$および$LiCoO_2$の３種混合物を用いた電池は$LiNiO_2$および$LiCoO_2$の使用に起因して、安全性が十分ではない問題がある。

【０００９】本発明は、このような課題を解決するためになされたもので、その目的は、ハイレートでの充放電が可能で、容量が高く、充放電サイクル耐久性に優れた高安全性の非水電解液二次電池用正極材料を用いた高エネルギー密度かつ高電流放電特性の良い非水電解液二次電池を提供することにある。

【００１０】

【課題を解決するための手段】上記目的を達成するため、本発明は、リチウム遷移金属複合酸化物を主成分とする正極活物質層を備えたリチウム二次電池において、上記リチウム遷移金属複合酸化物が、$Li_xNi_yMn_{1-y-z}M_zO_2$（ただし、ｘは０．９≦ｘ≦１．２、ｙは０．４０≦ｙ≦０．６０、ｚは０≦ｚ≦０．２であり、ＭはＦｅ，Ｃｏ，Ｃｒ，Ａｌ原子のいずれかから選択される。）で表されるリチウム－ニッケル－マンガン－Ｍ複合酸化物と、Ｆｄ３ｍスピネル構造を有し、$Li_pMn_2O_4$（ただし、ｐは１≦ｐ≦１．３である。）で表されるリチウム－マンガンスピネル複合酸化

物との混合物からなることを特徴としている。

【００１１】本発明において、上記リチウム−ニッケル−マンガン−M複合酸化物はR３−m菱面体構造であることが好ましい。なお、ｙが０．４０未満であると安定なR−３m菱面体構造をとりにくくなるので好ましくない。また、ｙが０．６０を超えると安全性が低下するので好ましくない。ｙは特に好ましくは０．４５〜０．５５が採用される。ｘは容量発現のため、$0.9 \leqq x \leqq 1.2$が採用される。

【００１２】上記リチウム−ニッケル−マンガンM複合酸化物に対し、さらにＦｅ，Ｃｏ，Ｃｒ，Ａｌのいずれかの原子を加えることにより、充放電サイクル耐久性、安全性、容量等の向上が図れる。M原子の添加量ｚは０〜０．２で、好ましくは０．０１〜０．１８、特に好ましくは０．０５〜０．１６である。

【００１３】本発明で用いるもう一方の上記リチウム複合酸化物は、Ｆｄ３ｍスピネル構造を有し、$Li_pMn_2O_4$（ただし、ｐは、$1 \leqq p \leqq 1.3$である。）で表されるリチウム−マンガンスピネル複合酸化物であるが、このマンガンスピネル中のマンガン元素を、マンガン以外のアルカリ土類金属元素や遷移金属元素をもって２〜１０モル％置換することにより、充放電サイクル耐久性を向上させることができる。マンガンスピネル中のマンガンの好ましい置換元素としては、マグネシウム、アルミニウム、鉄、クロムが選択される。

【００１４】本発明において、上記混合物中の上記リチウム−ニッケル−マンガン−M複合酸化物の含有量は３０〜７０重量％であることが好ましい。上記含有量が３０重量％未満であるとリチウム電池の容量が低下したり、充放電サイクル耐久性が低下するので好ましくない。また、上記含有量が７０重量％を超えるとハイレートでの放電容量が低下したり、放電平均電圧が低下するので好ましくない。特に好ましい上記含有量は４０〜６０重量％である。

【００１５】本発明において、上記複合酸化物の混合物粉末は、粉末のみを$1\ t/cm^2$の圧力でプレス充填したときの粉体プレス密度が$2.7\ g/cm^3$以上であることが好ましい。これによれば、混合物をスラリーとなして集電体アルミ箔に塗工・乾燥・プレスした際に体積当たりの容量を高くすることができる。特に好ましい粉体プレス密度は$2.9\ g/cm^3$以上である。$2.7\ g/cm^3$以上の粉体プレス密度は、混合物粉体の粒径分布を適正化することにより達成される。すなわち、粒径分布に幅があり、少粒径の体積分率が２０〜５０％であり、大粒径の粒径分布を狭くすること等により高密度化が図れる。

【００１６】本発明の混合物を用いると、混合に用いたそれぞれの単独のリチウム遷移金属複合酸化物を用いた場合より、ハイレートでの充放電が可能で、容量、安全性のバランスが向上した電池性能が発現できる。また、単独のリチウム遷移金属化合物からなり、かつ、混合に用いた遷移金属元素含量と同じである正極活物質を用いた場合より、容量と安全性並びに充放電サイクル安定性の優れた電池性能を得ることができる。かかる、物理的混合物の方が単独物質より優れる原因は明らかではないが、リチウム−ニッケル−マンガン−M複合酸化物（Ni／Mn＝０．６／０．４〜０．４／０．６）が特段に安全性が高く、容量の発現性が比較的良いため、混合により相乗効果が発現したものと考えられる。

【００１７】

【発明の実施の形態】本発明に用いる結晶構造が菱面体のR−３mからなる、$Li_xNi_yMn_{1-y-z}M_zO_2$（リチウム−ニッケル−マンガン−M複合酸化物）の製法としては、例えばマンガン化合物とリチウム化合物とニッケル化合物の混合物を不活性ガス雰囲気下あるいは大気中で固相法５００〜１０００℃焼成すること、５００〜８５０℃での溶融塩法が挙げられる。

【００１８】また、本発明に用いる結晶構造が菱面体層状岩塩型構造からなる、リチウム−ニッケル−マンガン−M複合酸化物は、例えばニッケル−マンガン−金属元素からなる複合酸化物あるいは複合水酸化物とマンガン化合物とリチウム化合物の混合物を酸素ガス含有雰囲気下で固相法５００〜１０００℃焼成すること、５００〜８５０℃のリチウム含有溶融塩中にニッケル−マンガン−金属元素M含有化合物を添加する溶融塩法により得ることができる。

【００１９】ニッケル源原料としては、酸化物（NiOなど）、水酸化物（NiOH）、オキシ水酸化物（NiOOH）などが挙げられる。マンガン源原料としては、酸化物（Mn_2O_3，MnO，MnO_2など）、これら酸化物の水和物、オキシ水酸化物などが挙げられる。マンガン源原料としては、３価のマンガンの化合物がより好ましい。これらのマンガン源原料は、単独で使用してもよく、２種以上を併用してもよい。

【００２０】金属元素（M）源原料としては、単体金属、水酸化物、酸化物、オキシ水酸化物、塩化物、硝酸塩等が使用される。これらの金属元素（M）源原料は、単独で使用してもよく、２種以上を併用してもよい。

【００２１】本発明の混合物の粉末に、アセチレンブラック、黒鉛、ケッチエンブラック等のカーボン系導電材と結合材を混合することにより正極合剤が形成される。結合材には、ポリフッ化ビニリデン、ポリテトラフルオロエチレン、ポリアミド、カルボキシメチルセルロース、アクリル樹脂等が用いられる。本発明の混合物の粉末と導電材と結合材ならびに結合材の溶媒または分散媒からなるスラリーをアルミニウム箔等の正極集電体に塗工・乾燥およびプレス圧延せしめて正極活物質層を正極集電体上に形成する。

【００２２】本発明のリチウム電池において、電解質溶液の溶媒としては炭酸エステルが好ましい。炭酸エステ

ルは環状、鎖状いずれも使用できる。環状炭酸エステルとしてはプロピレンカーボネート、エチレンカーボネート等が例示される。鎖状炭酸エステルとしてはジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、メチルプロピルカーボネート、メチルイソプロピルカーボネート等が例示される。

【００２３】本発明では上記炭酸エステルを単独でまたは２種以上を混合して使用できる。また、他の溶媒と混合して使用してもよい。また、負極活物質の材料によっては、鎖状炭酸エステルと環状炭酸エステルを併用すると、放電特性、サイクル耐久性、充放電効率が改良できる場合がある。また、これらの有機溶媒にフッ化ビニリデン－ヘキサフルオロプロピレン共重合体（例えばアトケム社カイナー）、フッ化ビニリデン－パーフルオロプロピルビニルエーテル共重合体を添加し、下記の溶質を加えることによりゲルポリマー電解質としてもよい。

【００２４】溶質としては、ClO_4^-、$CF_3SO_3^-$、BF_4^-、PF_6^-、AsF_6^-、SbF_6^-、$CF_3CO_2^-$、$(CF_3SO_2)_2N^-$等をアニオンとするリチウム塩のいずれか１種以上を使用することが好ましい。上記の電解質溶液またはポリマー電解質は、リチウム塩からなる電解質を上記溶媒または溶媒含有ポリマーに０．２～２．０ｍｏｌ／ｌの濃度で添加するのが好ましい。この範囲を逸脱すると、イオン伝導度が低下し、電解質の電気伝導度が低下する。より好ましくは０．５～１．５ｍｏｌ／ｌが選定される。セパレータには多孔質ポリエチレン、多孔質ポリプロピレンフィルムが使用される。

【００２５】本発明における負極活物質は、リチウムイオンを吸蔵、放出可能な材料である。これらの負極活物質を形成する材料は特に限定されないが、例えばリチウム金属、リチウム合金、炭素材料、周期表１４、１５族の金属を主体とした酸化物、炭素化合物、炭化ケイ素化合物、酸化ケイ素化合物、硫化チタン、炭化ホウ素化合物等が挙げられる。

【００２６】炭素材料としては、様々な熱分解条件で有機物を熱分解したものや人造黒鉛、天然黒鉛、土壌黒鉛、膨張黒鉛、鱗片状黒鉛等を使用できる。また、酸化物としては、酸化スズを主体とする化合物が使用できる。負極集電体としては、銅箔、ニッケル箔等が用いられる。

【００２７】本発明における正極及び負極は、活物質を有機溶媒と混練してスラリとし、該スラリを金属箔集電体に塗布、乾燥、プレスして得ることが好ましい。本発明のリチウム電池の形状には特に制約はない。シート状（いわゆるフイルム状）、折り畳み状、巻回型有底円筒形、ボタン形等が用途に応じて選択される。

【００２８】

【実施例】次に、本発明を具体的な実施例１～８および比較例１～４について説明するが、本発明はこれらの実施例に限定されない。

【００２９】《実施例１》硫酸ニッケルと硫酸マンガン（モル比１：１）混合水溶液に、アンモニア水と水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱・乾燥により、ニッケル－マンガン共沈水酸化物（ニッケル：マンガン原子比＝１：１）を得た。このニッケル－マンガン共沈水酸化物を５５０℃で大気中で焼成・粉砕し、ニッケル－マンガン酸化物粉末を得た。このニッケル－マンガン酸化物粉末と炭酸リチウム粉末を混合し、８００℃で窒素ガス雰囲気中で焼成・粉砕して平均粒径４μｍの$LiNi_{0.5}Mn_{0.5}O_2$を合成した。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｒ－３ｍ菱面体層状岩塩型構造であることが判った。また、電解二酸化マンガン粉末と炭酸リチウム粉末を乾式混合し、大気中で８００℃１５時間焼成して粉砕・分級して平均粒径７μｍの$Li_{1.05}Mn_2O_4$粉末を得た。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｆｄ３ｍスピネル構造であることが判った。$LiNi_{0.5}Mn_{0.5}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合し、この混合物粉末を１ｔ／cm^2の圧力で油圧プレスして体積と重量から粉体プレス密度を求めたところ、２．９０ｇ／cm^3であった。この混合物粉末とアセチレンブラックとポリフッ化ビニリデンとを８３／１０／７の重量比でＮ－メチルピロリドン加えつつボールミル混合し、スラリーとした。このスラリーを厚さ２０μのアルミニウム箔正極集電体上に塗布し、１５０℃にて乾燥してＮ－メチルピロリドンを除去した。しかる後にロールプレス圧延をして正極体を得た。セパレータには厚さ２５μの多孔質ポリエチレンを用い、厚さ３００μの金属リチウム箔を負極に用い負極集電体にニッケル箔を使用し、電解液には１Ｍ　$LiPF_6$／ＥＣ＋ＤＥＣ（１：１）を用いてコインセル２０３０型をアルゴングローブボックス内で組立た。そして、２５℃の温度雰囲気下において、１ｍＡで終止電圧４．３Ｖで充電し、定電流５ｍＡ（放電率１Ｃ）にて３．０Ｖまで放電して高電流放電特性を調べる一方、１ｍＡで終止電圧４．３Ｖで充電し、定電流１ｍＡ（放電率０．２Ｃ）にて３．０Ｖまで放電する充放電サイクル試験を２０回行ない、２回充放電後の初期放電容量と２０回充放電後の放電容量との比率から容量維持率を求めた。また、電池安全性評価のため、４．３Ｖ充電後のセルを解体し、正極を電解液溶媒とともに密閉容器に入れて試料となし、示差走査熱量測定装置を用い、昇温せしめた時の発熱開始温度を求めた。その結果、初期容量は１２４ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９２％、容量維持率は９３％、発熱開始温度は２２７℃であった。

【００３０】《実施例２》リチウム－ニッケル－マンガン複合酸化物のニッケルとマンガンの原子比を０．６０：０．４０とした$LiNi_{0.6}Mn_{0.4}O_2$と、

$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１３０ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９２％、容量維持率は９４％、発熱開始温度は２２１℃であった。

【００３１】《実施例３》リチウム－ニッケル－マンガン複合酸化物のニッケルとマンガンの原子比が０．５０：０．５０である$LiNi_{0.5}Mn_{0.5}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で４０：６０の割合で混合した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１２２ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９３％、容量維持率は９４％、発熱開始温度は２２０℃であった。

【００３２】《実施例４》リチウム－ニッケル－マンガン複合酸化物のニッケルとマンガンの原子比を０．５５：０．４５とした$LiNi_{0.55}Mn_{0.45}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で３０：７０の割合で混合した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１２１ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９４％、容量維持率は９４％、発熱開始温度は２２０℃であった。

【００３３】《実施例５》上記実施例１の硫酸ニッケルと硫酸マンガン（モル比１：１）混合水溶液に代えて、硫酸ニッケルと硫酸マンガンと硫酸コバルト（モル比９：９：２）混合水溶液を用いた他は、上記実施例１と同様にして正極活物質として平均粒径５μｍの$LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$を合成した。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｒ－３ｍ菱面体層状岩塩型構造であることが判った。$LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合し、この混合物粉末を１ｔ／ｃｍ^{2}の圧力で油圧プレスして体積と重量から粉体プレス密度を求めたところ、２．９５ｇ／ｃｍ^{3}であった。上記実施例１と同様にして正極体および電池を作製し特性を評価した。その結果、初期容量は１２８ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９３％、容量維持率は９５％、発熱開始温度は２２６℃であった。

【００３４】《実施例６》上記実施例１の硫酸ニッケルと硫酸マンガン（モル比１：１）混合水溶液に代えて、硫酸ニッケルと硫酸マンガンと硫酸クロム（モル比９：９：２）混合水溶液を用いた他は、上記実施例１と同様にして正極活物質として平均粒径５μｍの$LiNi_{0.45}Mn_{0.45}Cr_{0.1}O_2$を合成した。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｒ－３ｍ菱面体層状岩塩型構造であることが判った。$LiNi_{0.45}Mn_{0.45}Cr_{0.1}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合し、この混合物粉末を１ｔ／ｃｍ^{2}の圧力で油圧プレスして体積と重量から粉体プレス密度を求めたところ、２．９２ｇ／ｃｍ^{3}であった。上記実施例１と同様にして正極体および電池を作製し特性を評価した。その結果、初期容量は１２６ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９３％、容量維持率は９５％、発熱開始温度は２３０℃であった。

【００３５】《実施例７》上記実施例１の硫酸ニッケルと硫酸マンガン（モル比１：１）混合水溶液に代えて、硫酸ニッケルと硫酸マンガンと硫酸鉄（モル比９：９：２）混合水溶液を用いた他は、上記実施例１と同様にして正極活物質として平均粒径５μｍの$LiNi_{0.45}Mn_{0.45}Fe_{0.1}O_2$を合成した。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｒ－３ｍ菱面体層状岩塩型構造であることが判った。$LiNi_{0.45}Mn_{0.45}Fe_{0.1}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合し、この混合物粉末を１ｔ／ｃｍ^{2}の圧力で油圧プレスして体積と重量から粉体プレス密度を求めたところ、２．９０ｇ／ｃｍ^{3}であった。上記実施例１と同様にして正極体および電池を作製し特性を評価した。その結果、初期容量は１２３ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９３％、容量維持率は９４％、発熱開始温度は２３１℃であった。

【００３６】《実施例８》上記実施例１の硫酸ニッケルと硫酸マンガン（モル比１：１）混合水溶液に代えて、硫酸ニッケルと硫酸マンガンと硫酸アルミニウム（モル比９：９：２）混合水溶液を用いた他は、上記実施例１と同様にして正極活物質として平均粒径５μｍの$LiNi_{0.45}Mn_{0.45}Al_{0.1}O_2$を合成した。この粉末のＣｕＫαによるＸ線回折分析の結果、Ｒ－３ｍ菱面体層状岩塩型構造であることが判った。$LiNi_{0.45}Mn_{0.45}Al_{0.1}O_2$と、$Li_{1.05}Mn_2O_4$とを重量比で５０：５０の割合で混合し、この混合物粉末を１ｔ／ｃｍ^{2}の圧力で油圧プレスして体積と重量から粉体プレス密度を求めたところ、２．８７ｇ／ｃｍ^{3}であった。上記実施例１と同様にして正極体および電池を作製し特性を評価した。その結果、初期容量は１２４ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９３％、容量維持率は９４％、発熱開始温度は２３３℃であった。

【００３７】〈比較例１〉上記実施例１において使用した$LiNi_{0.5}Mn_{0.5}O_2$を単独で使用した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１２８ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は８５％、容量維持率は９２％、発熱開始温度は２３０℃であった。

【００３８】〈比較例２〉硫酸ニッケルと硫酸マンガン（モル比０．７０：０．３０）混合水溶液に、アンモニア水と水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱・乾燥により、ニッケル－マンガン共沈水酸化物（ニッケル：マンガン原子比＝０．７０：０．３

０）を得た。このニッケルーマンガン共沈水酸化物を５５０℃で大気中で焼成・粉砕し、ニッケルーマンガン酸化物粉末を得た。このニッケルーマンガン酸化物粉末と水酸化リチウム粉末を混合し、４８０℃で焼成し、さらに大気中で８００℃で焼成・粉砕して$LiNi_{0.7}Mn_{0.3}O_2$を合成した。この$LiNi_{0.7}Mn_{0.3}O_2$を単独で使用した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１６７ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は８６％、容量維持率は９１％、発熱開始温度は２００℃であった。

【００３９】〈比較例３〉上記実施例１において使用した$Li_{1.05}Mn_2O_4$を単独で使用した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１１７ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は９４％、容量維持率は９３％、発熱開始温度は２２０℃であった。

【００４０】〈比較例４〉硫酸ニッケルと硫酸マンガン（モル比０．２５：０．７５）混合水溶液に、アンモニア水と水酸化ナトリウム水溶液を加えて共沈させ、１５０℃で加熱・乾燥により、ニッケルーマンガン共沈水酸化物（ニッケル：マンガン原子比＝０．２５：０．７５）を得た。このニッケルーマンガン共沈水酸化物を５５０℃で大気中で焼成・粉砕し、ニッケルーマンガン酸化物粉末を得た。このニッケルーマンガン酸化物粉末と水酸化リチウム粉末を混合し、４８０℃で焼成し、さらに窒素雰囲気中で８００℃で焼成・粉砕して$LiNi_{0.25}Mn_{0.75}O_2$を合成した。この$LiNi_{0.25}Mn_{0.75}O_2$を単独で使用した他は、上記実施例１と同様に正極体および電池を作製し特性を評価した。その結果、初期容量は１１９ｍＡｈ／ｇ、１Ｃ容量／０．２Ｃ容量は８３％、容量維持率は８７％、発熱開始温度は２３０℃であった。

【００４１】参考として、次表に上記実施例１～８および比較例１～４で用いた複合酸化物と評価結果をまとめて示す。

【表１】

	第1活物質	混合比(%)	第2活物質	混合比(%)	容量(mAh/g)	1C容量/0.2C容量(%)	容量維持率(%)	発熱開始温度(℃)
実施例1	$LiNi_{0.50}Mn_{0.50}O_2$	50	$Li_{1.05}Mn_2O_4$	50	124	92	93	227
実施例2	$LiNi_{0.60}Mn_{0.40}O_2$	50	$Li_{1.05}Mn_2O_4$	50	130	92	94	221
実施例3	$LiNi_{0.50}Mn_{0.50}O_2$	40	$Li_{1.05}Mn_2O_4$	60	122	93	94	220
実施例4	$LiNi_{0.55}Mn_{0.45}O_2$	30	$Li_{1.05}Mn_2O_4$	70	121	94	94	220
実施例5	$LiNi_{0.45}Mn_{0.45}Co_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	128	93	95	226
実施例6	$LiNi_{0.45}Mn_{0.45}Cr_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	126	93	95	230
実施例7	$LiNi_{0.45}Mn_{0.45}Fe_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	123	93	94	231
実施例8	$LiNi_{0.45}Mn_{0.45}Al_{0.10}O_2$	50	$Li_{1.05}Mn_2O_4$	50	124	93	94	233
比較例1	$LiNi_{0.50}Mn_{0.50}O_2$	100	―		128	85	92	230
比較例2	$LiNi_{0.70}Mn_{0.30}O_2$	100	―		167	86	91	200
比較例3	―		$Li_{1.05}Mn_2O_4$	100	117	94	93	220
比較例4	$LiNi_{0.25}Mn_{0.75}O_2$	100	―		119	83	87	230

【００４２】
【発明の効果】以上説明したように、リチウム遷移金属複合酸化物を主成分とする正極活物質層を備えたリチウム二次電池において、リチウム遷移金属複合酸化物に、本発明の複合酸化物の混合物を用いることにより、ハイレートでの充放電が可能で、混合に用いたそれぞれの単独のリチウム遷移金属複合酸化物を用いた場合より、容量、安全性のバランスが向上した電池性能が発現できる。

【００４３】また、単独のリチウム遷移金属化合物からなり、かつ、混合に用いた遷移金属元素含量と同じである正極活物質を用いた場合より、容量と安全性並びに充

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放電サイクル安定性の優れた電池性能を得ることができる。

フロントページの続き

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